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Water outgassing from PBX-9502 powder by isoconversional thermal analysis

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Abstract

Temperature programmed desorption/decomposition (TPD) were performed on PBX-9502 after 3 hours of vacuum pump. TPD data were analyzed by the technique of isoconversional analysis to obtain outgassing kinetics and moisture content of PBX-9502 powder as well as to construct water outgassing models for PBX-9502 powder as a function of time and temperature. Following 3 hours of vacuum pump, dry storage of PBX-9502 at 300K, quickly gives rise to 180-330 ppm moisture in the first few years. Thereafter, the moisture outgassing continues at a much slower rate, totaling only to ~ 210-380 ppm after 100 years of storage.

Introduction:

In an effort to understand the nature of the moisture outgassing in PBX-9502, we have measured moisture content and outgassing kinetics in PBX-9502 by the experimental technique of TPD and the isoconversional thermal analysis. The results of these measurements were then used to construct moisture outgassing models for PBX-9502 in a dry environment (following 3 hours of vacuum pump).

Experimental Method:

For a typical TPD experiment, PBX-9502 powder (< 10 mg) was wrapped inside a Pt foil envelope. The side of the envelope facing the mass spectrometer was perforated with pin holes over its entire surface. The loaded foil was attached to a sample holder by way of mechanical clamps and transferred into an ultrahigh vacuum (UHV) chamber with a base pressure of 10^{-6} Pa (4 x 10^{-7} Pa in the mass spectrometer chamber) through a differentially pumped load lock. The sample temperature was measured using a type K thermocouple inserted between the Pt envelope front surface and one of the clamps holding the envelope. The sample was then pumped in the UHV chamber for 3 hours to remove H_2O molecules that were loosely bonded to the powder. Heating of the samples was done by passing current through a tungsten coil located 2 mm behind the samples. The detector chamber is equipped with a quadrupole mass spectrometer (QMS) and has been described in detail elsewhere [1].

Analysis Technique:

The rate equation for a solid-state reaction can be approximated by [2]:

$$\frac{d\alpha}{dt} = k.f(\alpha) = \upsilon.e^{-\frac{E}{RT}}.f(\alpha) \tag{1}$$

where t is time; α is the reacted fraction (0 to 1); k is the rate constant; υ is the pre-exponential factor which includes many constants describing the initial state of the sample such as the shape factors of initial particles, molecular mass, density, stoichiometry, active surface factors, number of lattice imperfections, and so forth; E is the activation energy for the rate controlling process; R is the gas molar constant, T is temperature in Kelvin; and $f(\alpha)$ is an analytical function determined by the rate-limiting reaction mechanism.

With a heating rate of $\beta = dT / dt$:

$$\frac{d\alpha}{dT} = \left[\frac{\upsilon}{\beta} \cdot f(\alpha)\right] \cdot e^{-\frac{E}{RT}} \tag{2}$$

Taking the natural logarithm on both sides of equation (1) yields:

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln\{\upsilon f(\alpha)\} \tag{3}$$

A plot of *ln(dα/dt)* vs. T^{-1} at some α value for a set of β values has the slope $-E/R$ [3]. A plot of E vs. α is thus obtained by repeating the above procedure at other chosen α values between 0 and 1. This kinetic extraction procedure was first proposed by Friedman [3]. Note that both E and $\{\upsilon f(\alpha)\}$ can be obtained the Friedman method based on equation (3). The time prediction, t_α, for a specific conversion α to be reached at the isothermal temperature T_o can be obtained from the rate equation (1) as following [1, 4]:

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^{\alpha} \frac{d\alpha}{\{\upsilon f(\alpha)\} e^{\frac{-E}{RT_o}}} \tag{4}$$

Note that no assumption needs to be made about the pre-exponential factor υ or the rate limiting step $f(\alpha)$ in the isoconversional thermal analysis. As long as E and $ln\{\upsilon f(\alpha)\}$ can be obtained from the slope and the intercept of the $ln(d\alpha/dt)$ vs. $1/T$ plot, equation (4) can be employed to make kinetic prediction. The ability to make kinetic measurements and prediction without any prior knowledge of υ or $f(\alpha)$ is the strength of the isoconversional thermal analysis technique which is very suitable for kinetic problems involving unknown and complex processes with continually varying kinetic parameters[1]. Even in the case if a knowledge of the reaction is known in detail, the isoconversional thermal analysis can still serve to check on the kinetics derived from a model dependent analysis[4].

Results & Discussion:

The TPD spectra of PBX-9502 at different heating rates after 3 hours of vacuum pump are presented in Fig. 1. The spectra appear to shift toward higher temperatures with faster heating rates. This is expected for processes with a positive activation energy barrier.
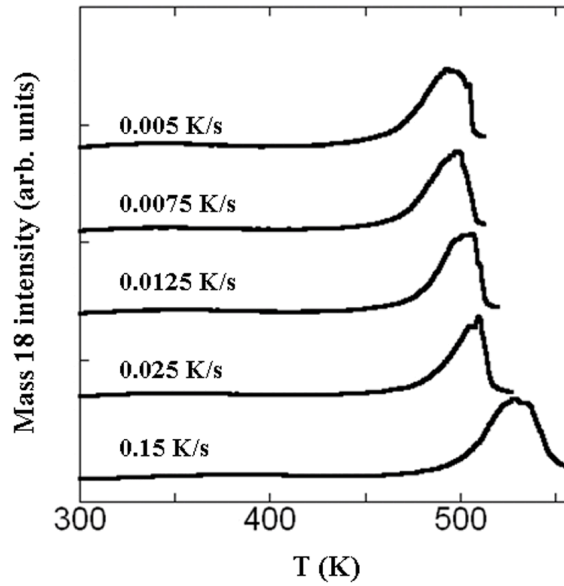

Fig. 1: TPD spectra of PBX-9502 at various heating rates.

The plot of E vs. α obtained from the isocoversional analysis technique described above is shown in Fig. 2. The activation energy barrier for moisture outgassing is seen to increase from around 15 kcal/mol at $\alpha = 0.1$ to greater than 40 kcal/mol at $\alpha = 0.2$ and pretty much hovers above 40 kcal/mol until $\alpha = 0.8$. Thereafter, the activation energy barrier sharply drops to ~ 30 kcal/mol when α reaches 0.9. The nature of the derivative of the Friedman isoconversional technique implies that the E vs. α plot tends to be artificially unstable, exploded, or generally behaves suspiciously in the $0 < \alpha < 0.1$ (near the beginning of a reaction) and $0.9 < \alpha < 1.0$ (near

the end of a reaction) range. As a result, only the values of E corresponding to $0.1 \leq \alpha \leq 0.9$ are shown in Fig. 2.
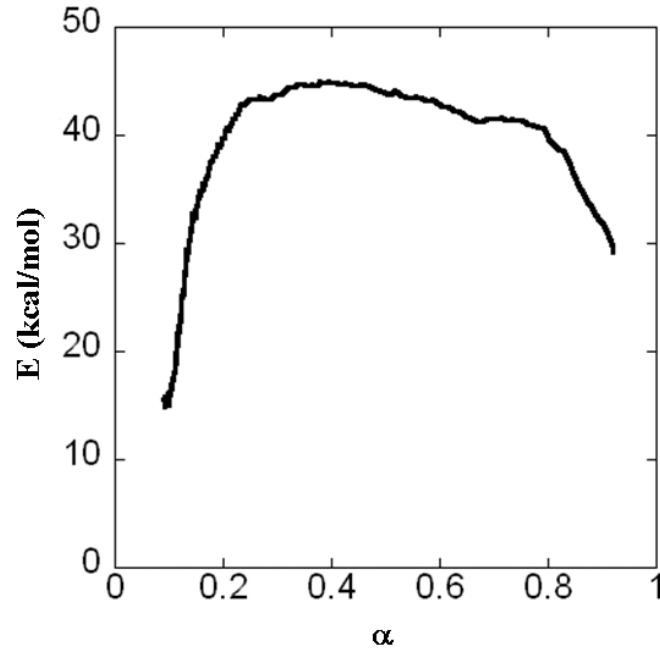

Fig. 2: The E vs. α plot obtained from the TPD spectra in Fig. 1 according to the isoconversional thermal analysis.

The kinetic predictions of moisture outgassing as a function of time, at any temperature, can now be made with the help of equation (4). Such a prediction for the case of moisture outgassing from PBX-9502 (after 3 hours of vacuum pump) at 300K and 343K are presented in Figs. 3 & 4, respectively.
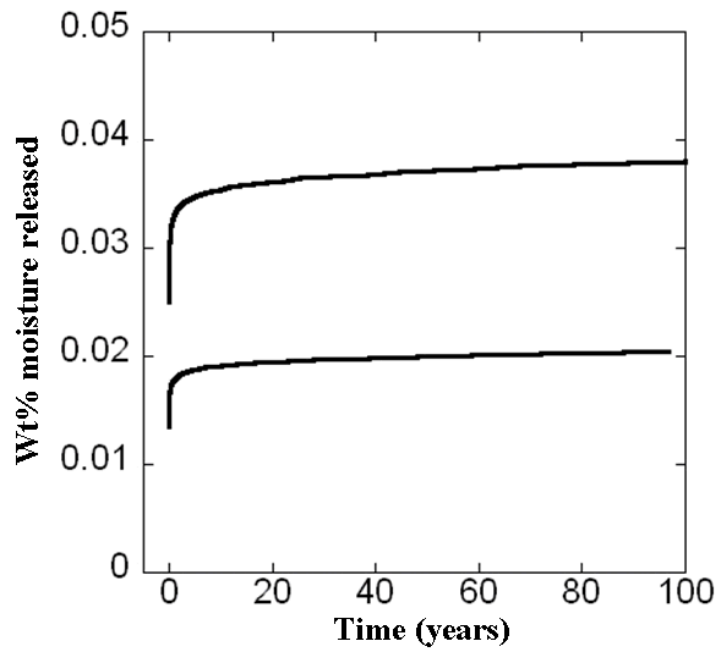

Fig. 3: Moisture outgassing prediction for PBX-9502 (after 3 hours of vacuum pump*)* at 300K.
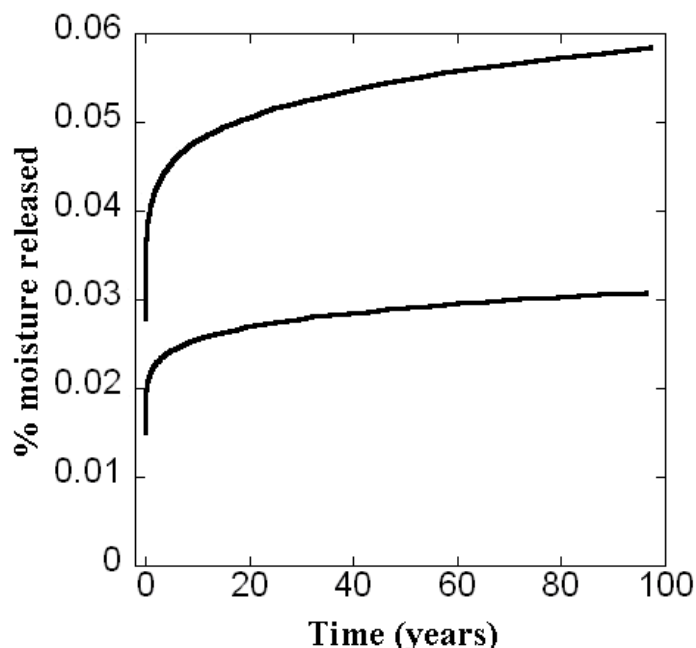
Fig. 4: Moisture outgassing prediction for PBX-9502 (after 3 hours of vacuum pump*)* at 343K.

From Fig. 3, the moisture outgassing from PBX-9502 (after 3 hours of vacuum pump) quickly rises to between 180-330 ppm with the first few years of dry storage but slows down thereafter. Much of the physisorbed water (water molecules hydrogen-bonded to each other) has already pumped out during the 3 hours of vacuum pump. The quick rise of moisture outgassing during the first few years of dry storage may be due to the desorption of left-over physisorbed water and the slow increase thereafter may be due to the desorption of chemisorbed water. The total moisture outgassing from PBX-9502 ranges between 210 ppm and 380 ppm after 100 years of dry storage at 300K. At 343K, the total moisture outgassing from PBX-9502 ranges between 310 ppm and 580 ppm after 100 years (see Fig. 4).

Conclusion and discussion:
The water outgassing kinetics of PBX-9502 powder (after 3 hours of vacuum pump) were measured by the TPD technique. Quantitative moisture outgassing from PBX-9502 in a dry environment at any temperature as a function of time can be constructed from the measured kinetics based on the isoconversional thermal analysis and has been demonstrated in this report. It is also important to point out that the moisture outgassing in "hot-pressed" PBX-9502 may be significantly different (most likely less) than that found in the powder. In addition, diffusion of water in "hot-pressed" PBX-9502 may also slow down the outgassing rate. Re-absorption of moisture after the "hot-pressed" action may also make the water outgassing properties in "hot-pressed" PBX-9502 deviates from powder samples presented here. However, the moisture outgassing kinetic measurements and predictions presented in this technical report should serve to give an order of magnitude trend in the moisture outgassing properties of PBX-9502 in general.

Acknowledgement:

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